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Chemical, Structural and Optical Properties of ē-Beam Evaporated Tungsten Diselenide Polycrystalline Thin Film

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Polycrystalline thin films of tungsten dieseline were prepared by using rarely reported technique of electron beam evaporation for transition metal dichalcogenides. High purity (99.999 %) reacted compound was used as starting material for the preparation of WSe_2 thin films. Various parameters and conditions are outlined which were used for deposition of thin films. The prepared films were characterized using EDAX spectrum, X-ray diffraction, Electron diffraction, Scanning electron microscopy and optical absorption spectroscopy methods. The as grown films were found to be partially transparent, uniform and well adherent. Uniformity was confirmed by SEM. WSe_2 film was found in stoichiometric proportion. XRD pattern as well as TEM images revealed the fact that the deposited films are polycrystalline in nature having hexagonal structure. From the study of optical absorption spectra it is found that the prepared films show direct allowed transition with optical band gap of 1.89 eV. The results are in good agreement with the earlier published data of WSe_2 thin films deposited by different techniques.

Keywords: ē-Beam Evaporation, WSe_2 Thin Films, Structural analysis, Optical Studies, SEM, TEM.

PACS numbers: 68.55aj, 73.90 + F

1. INTRODUCTION

The various chalcogenide thin films like WSe_2, $MoSe_2$, WS_2, CdS, CdSe, and SnSe have been prepared and characterized for structural, optical and electrical studies by above mention technique [1-9]. Transition metal dichalcogenides like WSe_2, $MoSe_2$ etc. can be used to convert solar energy to electrical energy efficiently in the thin film structure [10]. Tungsten diselenide (WSe_2) single crystals and thin films have attractive properties like bandgap in the range of 1 – 2 eV which is most suitable range of energy to tap solar spectrum for soalr cell applications. There have been several methods like chemical vapour deposition (CVD), R. F. Sputtering, Spray Pyrolysis, Electrodeposition, Solid reaction, Chemical bath deposition (CBD) etc. [1, 11-14] which have been reported for the preparation of polycrystalline thin films of tungsten diselenide.

Present paper reports the results of our investigations regarding deposition of WSe_2 thin films using electron beam evaporation technique and chemical, structural and optical characterization of prepared films. The preparative parameters like, vacuum condition, deposition rate, thickness, deposition temperature is reported in detailed in this paper.

2. EXPERIMENTAL DETAILS

Thin films of 1732 Å were deposited on chemically and ultrasonically cleaned glass substrates with the help of 3 kWatt 180° ē-beam source attached to a box-coater vacuum system (BC-300, Hindhivac-Banglore). All the gadgets of the vacuum chamber were first cleaned by acetone.

2.1 Substrate Cleaning

The deposition was done on glass slides of 4 inch × 2 inch dimensions. These substrates were cleaned by ultrasonic vibrations followed by washing successively with detergent and acetone.

2.2 Source Materials

Analytical grade high purity reacted tungsten diselenide powder (99.999 %) was used to prepare thin films and it was placed in well cleaned water cooled copper crucible.

The cleaned substrates were fixed on the substrate holder and digital quartz crystal sensor was placed in close vicinity to them for the in situ thickness measurements. The chamber was evacuated at a pressure of 0.5×10^{-5} Torr by the combination of rotary and diffusion pump. When vacuum of 10^{-6} Torr was attained in the vacuum chamber, the emission current of filament was gradually raised to generate electron beam which is accelerated toward the water cooled crucible with the help of magnetic field. The accelerated electrons lose their energy by colliding to powdered source material and generate heat to raise the temperature in excess of the melting point of WSe_2. This allowed the evaporation of WSe_2 material. The rate of deposition was kept between 1 – 3.5 $Å s^{-1}$ till the final thickness of 1.732 kÅ of deposited films was attained.

2.3 Characterization of WSe_2 Thin Film

The thickness of deposited thin films was measured by in situ digital quartz crystal monitor (Hi-Tech DTM 101). The JEOL JSM 5410 SEM with an Oxford Link Isis-Energy Dispersive X-ray Spectrometer (EDS) was used for the chemical characterization and electron microscopy. The X-ray diffraction analysis of WSe_2 thin

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film has been carried out at 303 K using X-Ray Diffractometer (D8 Advance BRUKER AXS) with CuKα radiation of wave length 1.54 Å.

For TEM studies, films were deposited simultanously on freshly cleaved NaCl crystals also. The optical characterization of films were carried out using the UV-VIS-NIR spectrophotometer (Perkin Elmer-USA, Model: Lambda 19) in the range of 200 nm to 2500 nm wavelength.

3. RESULTS AND DISCUSSION

3.1 Stoichiometric Analysis

EDAX spectrum (Fig. 1(a)) confirmed that the deposition of WSe_2 films comprised of W and Se along with presence of oxygen content. The reason of presence of Oxygen in deposited films may be due to poor level of vacuum of the order of 0.5×10^{-5} Torr. No other elements were observed within the limits of sensitivity. Neglecting the oxygen contents, the chemical formula assigned to the deposited films can be $W_{0.94}Se_{2.06}$.

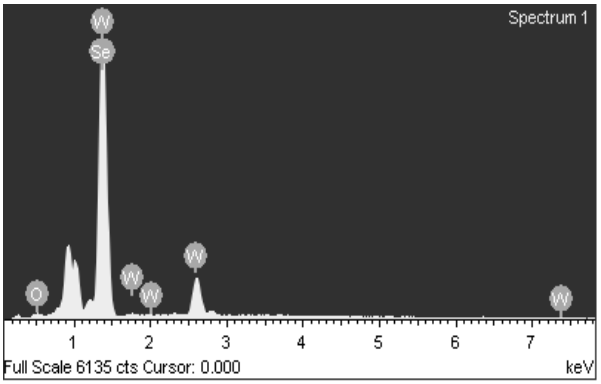


Fig. 1 – EDAX spectrum for WSe_2 thin film

Table 1 – Composition (Wt %) of WSe_2 Thin Film

Element	Weight%		Chemical Formula	
	EDAX	Expected	EDAX	Expected
O	5.13	0.0	$W_{0.94}Se_{2.06}$ (Neglecting oxygen content)	WSe_2
Se	43.81	46.21		
W	51.06	53.79		
Totals	100.00	100.00		

3.2 Crystallographic and Morphological Studies

The XRD pattern of WSe_2 thin film is shown in Fig. 2. Comparison of observed '*d*' values with standered '*d*' values confirms that ē beam evaporated thin film shows hexagonal structure (JCPDS-38-1388). The XRD pattern shows the highest intensity reflection peak at $2\theta = 13.96°$ with $d = 6.33$ Å (002). The diffused background is due to amorphous glass substrate. Along with (002) planes (103), (006), (008) planes were observed.

The lattice parameters '*a* and *c*' of WSe_2 film were found to be 3.25 Å, and 12.97 Å respectively. These values are in good agreements with the earlier reported [1, 15, 16]. The crystallite size was calculated by using Scherrer formula for highest intensity peaks. The crystallite size of WSe_2 thin film was found to be 59.31 Å. The crystallographic data are shown in Table 2(a). Table 2(b) shows the comparison of parameters of thin film of WSe_2 deposited using different techniques.

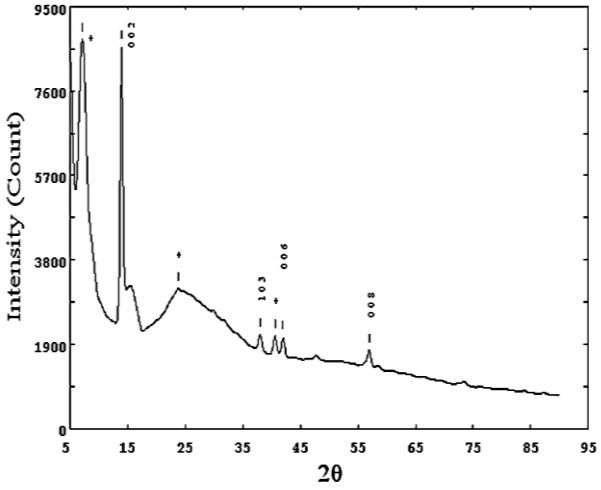


Fig. 2 – XRD diffrectogram for WSe_2 thin film

Table 2(a) – Crystallographic data of WSe_2 Thin Film

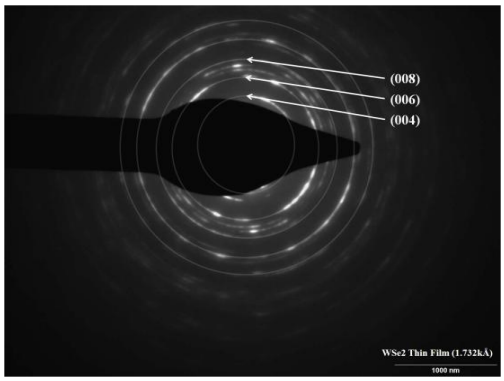
d- Values (Å)		hkl planes		Grain Size (Å)	Cell Parameters (Å)
Observed	TEM	XRD	TEM		
6.33		002		59.31	$a = b = 3.25$ $c = 12.97$
2.36	3.28	103	004	62.26	
2.14	2.21	006	006	33.78	
1.61	1.78	008	008	64.80	

Table 2(b) – Crystallographic data of WSe_2 thin films deposited by various techniques

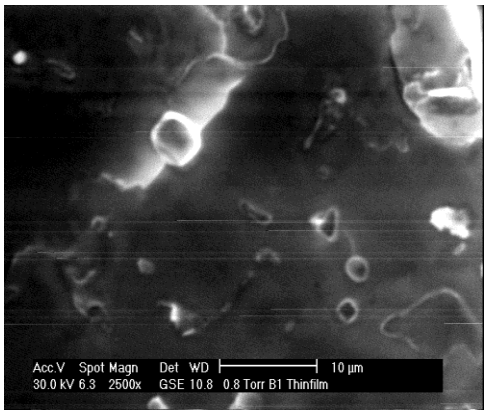
Deposition Technique	Optical Bandgap (eV)	Grain Size (Å)	Cell Parameters (Å)	Ref.
ē-beam Evaporation Technique (Present case)	1.89	59.31	$a = 3.25$ $c = 12.97$	
chemical synthetic route	1.48	159	$a = 3.28$ $c = 13.00$	[1]
Sputtering	1.91	450	--------	[17]
Synthesis by tarnishing	1.25	50 – 100	$a = 3.29$ $c = 13.1$	[18]
Electrodeposition.	1.46	2 – 15	$a = 3.35$ $c = 12.59$	[19]

The electron diffraction pattern of WSe_2 thin film (Fig. 3(a)) shows sharp rings corresponding to $d = 3.28$ Å, 2.21 Å, 1.78 Å with (004), (006), (008) planes respectively. This again confirms the hexagonal phase in the prepared films.

The SEM micrograph of WSe_2 thin film is shown in Fig. 3(b). It can be seen from here that the WSe_2 film is almost homogenous with small cracks and pinhole with stacked layer type features.



a



b

Fig. 3 – Electron diffraction image (a) SEM micrograph (b) for WSe_2 thin film

3.3 Optical Studies

The optical absorption spectra of tungsten diselenide films deposited onto glass substrates were studied at room temperature in the wavelength of 200 – 2500 nm. The optical study shows that the film is highly absorbing in nature in the energy range 1.7 – 3.3 eV and it show the presence of absorption edge.

The optical band gap 'E_g' was determined from variation of $(\alpha hv)^2$ with photon energy hv (Fig. 4). The linear nature of plot indicates the existence of direct transition and its extrapolation to energy axis ($\alpha = 0$) gives bandgap of 1.89 eV for WSe_2 films which is in good agreement with values reported earlier [1, 17].

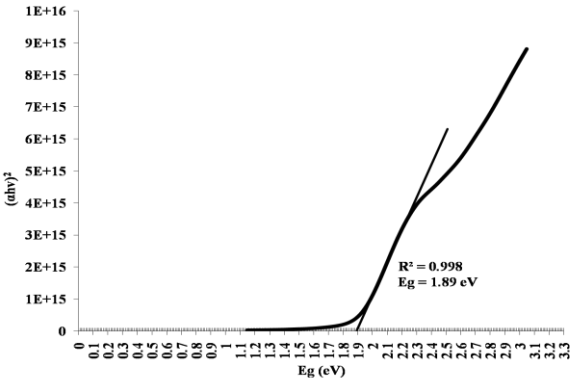


Fig. 4 – Plot of $(\alpha hv)^2$ vs. photon energy hv

4. CONCLUSION

WSe_2 thin film can be deposited by using ē-beam evaporation technique onto non-conducting glass. The X-ray diffraction revels that the films are polycrystalline in nature and posses hexagonal structure and it is confirmed against TEM studies also. The SEM micrograph shows the uniformity of film. Optical study shows that WSe_2 film has optical absorption coefficient. The direct bandgap obtained are 1.89 eV for film.

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